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(19)

(54) VINYL CHLORIDE RESIN COMPOSITIONS

(71) We, KANEKA FUCHI KAGAKU KOGYO KABUSHIKI KAISHA, a Corporation organized and existing under the laws of Japan of 3, 3-chome, Nakanesima, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

5 10 This invention relates to a vinyl chloride resin composition having favorable workability and physical properties.

15 Polyvinyl chloride has been widely used in industry due to its excellent physical and chemical properties. Polyvinyl chloride does, however, have a defect in workability since its working temperature approaches its temperature of thermal decomposition and a long time is required to obtain a fused mass of the 20 material. Furthermore, polyvinyl chloride has some defects in workability during secondary treatment of surfaces after extrusion, moulding or kneading of fused starting materials at working temperatures.

25 Many techniques have been tried for overcoming these problems. They consist essentially in addition of plasticizers, copolymerization of vinyl chloride with other monomer or addition of other resins to polyvinyl chloride, but these techniques have problems. So far, it has not been possible to obtain a sufficient improvement in workability and at the same time maintain the excellent physical and chemical properties of polyvinyl chloride. 30 For example, addition of plasticizers and copolymerization of vinyl chloride with other monomer results in a change in the physical properties. When other resin substances are added to polyvinyl chloride, the melt viscosity of polyvinyl chloride and also the working temperature is lowered. Although the fluidity of polyvinyl chloride improves by this addition, the gelatinization of polyvinyl chloride is insufficient, so that transparent articles are in- 40

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 ferior in physical properties to polyvinyl chloride which has been sufficiently gelatinized. Although a resinous substance which elevates the melt viscosity of polyvinyl chloride is known, the addition of such a resinous substance produces some non-gelatinized substances known as "fish eye" which spoils the appearance of articles formed therefrom.

The object of this invention is to provide compositions having excellent workability by overcoming the said surface defects or secondary workability of the article by accelerating the gelatinization of vinyl chloride resins, while maintaining the desirable properties of vinyl chloride resins.

According to the present invention, there is provided vinyl chloride resin composition comprising:

A. 100 parts by weight of a vinyl chloride resin which comprises polyvinyl chloride, a copolymer having at least 80% vinyl chloride with a monomer copolymerizable therewith, or a post-chlorinated polyvinyl chloride, or a combination thereof;

B. 0.1 to 100 parts by weight of a two stage polymerization product obtained by polymerizing (I) 50 to 99 parts by weight of methyl methacrylate or a first monomeric mixture comprising a major proportion of methyl methacrylate, and a minor proportion of acrylic acid ester and/or methacrylic acid ester, excluding methyl methacrylate, and then polymerizing in the presence of the resulting polymer latex (II) 50 to 1 parts by weight of a second monomeric mixture comprising a major proportion of acrylic acid ester and/or methacrylic acid ester, excluding methyl methacrylate, and a minor proportion of methyl methacrylate, wherein said first and second monomeric mixtures comprise other monomers of up to 20 weight percent of each such total monomer mixture.

The component B, can be prepared by the following two methods.

(1) At first methyl methacrylate only, or a monomeric mixture containing a major amount of methyl methacrylate is subjected to the emulsion polymerization, and then in the presence of the resulting polymer latex a mixture containing a major proportion of an acrylic acid ester and/or a methacrylic acid ester exclusive of methyl methacrylate and a minor proportion of methyl methacrylate is polymerized (two-staged polymerization product).

(2) A homopolymer of methyl methacrylate, or a copolymer containing a major amount of methyl methacrylate which is obtained by emulsion polymerization and a minor proportion of acrylic or methacrylic acid ester, excluding methyl methacrylate, is mixed in the latex state with a copolymer containing a major amount of an acrylic acid ester and/or a methacrylic acid ester exclusive of methyl methacrylate and a minor proportion of methyl methacrylate, which is obtained by the emulsion polymerization, and the mixture is coagulated (mixture of polymers blended in the latex state). Each of the products prepared by comparative prior methods other than the above methods, for instance, a) an ordinary polymerization method in which all the monomers constituting component (B) are copolymerized at random (random copolymers), b) a method where the monomers constituting constituent (II) are subjected to the emulsion polymerization and then the monomers constituting constituent (I) are polymerized in the presence of the resulting polymer latex (contrary two-staged polymerization products), and c) a method where the monomers constituting constituent (I) and the monomers of constituent (II) are copolymerized separately, the resulting copolymer latices are coagulated, and then they are blended in the powdery state (powdery mixtures), is defective in workability and transparency.

Although it has not been made clear how the fine structure of polymer (B) influences the resulting vinyl chloride resin composition, it seems that when fine particles of constituent (II) comprising as the main ingredient an acrylic acid ester and the like and having a low softening temperature are attached around fine particles of polymethyl methacrylate, or constituent (I) containing methyl methacrylate in the major amount and having a high softening temperature, and these copolymer particles in such state are mixed with a vinyl chloride resin, gelation is accelerated and an effect of complete gelation is attained. Such phenomena are apparent from experimental results shown in the following Tables 1 and 2.

Examples of acrylic acid esters and methacrylic acid esters exclusive of methyl methacrylate, which are starting materials for constituents (I) and (II) of the two-staged polymerization product or polymeric mixture

formed in the latex state (B), are methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethyl-hexyl acrylate, chloroethyl acrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethyl - hexyl methacrylate and chloroethyl methacrylate. These compounds may be used singly or in the form of admixtures of two or more of them. Use of methyl acrylate, ethyl acrylate, n-butyl acrylate, ethyl methacrylate and n-butyl methacrylate is especially preferred.

Parts of methyl methacrylate and acrylic acid esters and/or methacrylic acid esters exclusive of methyl methacrylate to be used for constituents (I) and (II) may be replaced by other monomers copolymerizable therewith without changing the ratios of the monomers. In order not to reduce the merits of the composition of this invention, the amount of such other monomer is less than 20% based on the constituent (I) or (II). As such third monomer there may be exemplified unsaturated nitriles (such as acrylonitrile and methacrylonitrile), vinyl esters (such as vinyl acetate and vinyl propionate), and monomers containing in the molecule two or more double bonds (such as monoethylene glycol dimethacrylate, diethylene glycol dimethacrylate, and polyethylene glycol dimethacrylate). These monomers may be used singly or in admixtures of two or more of them.

Better results are obtained with use of the two-staged polymerization product or polymeric mixture (B) having a degree of polymerization exceeding a certain level, when it is incorporated into a vinyl chloride resin. Although a preferred degree of polymerization of the component (B) varies, in general, depending on the composition and the degree of polymerization of the vinyl chloride resin, it is advantageous to use the component (B) having a specific viscosity, measured at 30°C. on a benzene solution of the polymer concentration of 0.4g/100cc, of at least 0.1, preferably at least 0.5.

It is well known to knead polymethyl methacrylate with a vinyl chloride resin. However, since the softening temperature of polymethyl methacrylate is too high, sufficient dispersion of polymethyl methacrylate cannot be attained under ordinary processing conditions for vinyl chloride resins and great portions remain ungelled. If the dispersion of polymethyl methacrylate is effected under severe processing conditions to accomplish the gelation, the resulting vinyl chloride resin is not applicable to practical use because of thermal degradation. When polymethyl methacrylate, whose thermal fluidity is increased by the reduction of the degree of polymerization, is kneaded with a vinyl chloride resin, even although there remains no ungelled portion, the improved workability of the vinyl chloride resin is not

attained, and therefore, gelation-accelerating property, surface states and secondary processability of the product are not improved.

It is also known to knead a random copolymer of methyl methacrylate and an acrylic acid ester with a vinyl chloride resin. The purpose of such a method resides in attaining complete gelation in the composition by employing a copolymer having a softening temperature lower than that of polymethyl methacrylate. If the amount of the acrylic acid copolymerized is small, ungelled portions remain in the kneaded product with the vinyl chloride resin. On the other hand, if the amount of the acrylic acid is large, the transparency of the vinyl chloride resin is reduced. Thus it is impossible to solve both problems coincidentally.

When only the constituent (I) of the polymer (B) in the composition of this application is used and kneaded with a vinyl chloride resin, the resulting composition is defective with respect to occurrence of ungelled portions. However, when the two-staged polymerization product or polymeric mixture formed in the latex state (B) comprising the constituent (II) as well as the constituent (I) is kneaded with a vinyl chloride resin, the above defect is overcome and there is obtained a composition characterized by a very short time for gelation without occurrence of any ungelled portion and having a good transparency. Further, in the composition there are retained excellent physical and chemical properties inherent to vinyl chloride resins. Still further, addition of the polymer (B) gives a smooth and lustrous surface to the product, and the product exhibits various merits at the secondary processing. For instance, it can be easily drawn deep at the time of vacuum molding. When only the constituent (II) is incorporated into a vinyl chloride resin, occurrence of ungelled portions can be prevented but the resulting composition is semi-transparent or opaque. Further, the composition is inferior in the gelation-accelerating effect. When the component (B) is incorporated in an amount exceeding 100 parts by weight of the polymerization product, the resulting composition is inferior in flame resistance and chemical resistance. At the component (B) content of less than 0.1 part, substantial improvement of workability is not attained.

The use of a two-staged polymerization product or polymeric mixture (B) in which the amount of the constituent (II) is larger than the amount of the constituent (I) is not preferred, because the resulting vinyl chloride resin composition is inferior in transparency.

For obtaining a vinyl chloride resin composition which is free of ungelled portions and is also suitably accelerated for gelation to a suitable degree, it is necessary for the constituent (II) to have a good compatibility with the vinyl chloride resin (A) and the

constituent (I) of the polymer (B) and have a considerably lower softening temperature than those of both (A) and constituent (I). For keeping a lower softening temperature in the constituent (II) it is essential that the amounts of the monomers are maintained, for if the amount of the methyl methacrylate should become larger than the amount of the other acrylic ester, there is formed a random copolymer similar to the product obtained by the above-mentioned comparative method, and the resulting composition comprises ungelled portions.

The incorporation of the two-staged polymerization product or polymeric mixture (B) into the vinyl chloride resin (A) may be accomplished by customary methods, and the way of the incorporation is not critical.

In the emulsion polymerization to obtain constituents (I) and (II) of the two-staged polymerization product or polymeric mixture (B), any known emulsifiers can be used, and water-soluble, oil-soluble and redox type polymerization initiators can be used. The degree of polymerization can be optionally adjusted by choosing a suitable combination of the polymerization temperature and chain transfer agent according to a customary technique.

The resulting vinyl chloride resin composition can be used for molding with or without stabilizers, lubricants, impact resistance enforcing agent, plasticizers, coloring agents, fillers, blowing agents and other additives.

The following is a description by way of example only of methods of carrying the invention into effect.

Example 1.

Into a reactor equipped with a stirrer, there is put a solution consisting of sodium dodecylbenzenesulfonate (2 parts), ammonium persulfate (0.1 part), and water (200 parts). The reactor and contents are deoxygenated and the solution is stirred at 60°C. Methyl methacrylate (80 parts) is added thereto over 4 hours. After addition of the monomer, the resultant mixture is stirred with heating for an hour, whereby the polymerization is completed substantially. A mixture of ethyl acrylate (13 parts) and methyl methacrylate (7 parts) is added thereto over a period of an hour, and the mixture is kept at 60°C for 1.5 hours and then cooled. A 99.5% conversion was obtained. The latex is salted out with sodium chloride, filtered, washed with water, and dried to give the polymer (1) (98 parts). The specific viscosity of the polymer sample (1) is 1.60, measured in benzene solution (0.4g/100 ml) at 30°C.

Similar procedures are effected to give polymers (2) to (4) as comparative examples. The polymer (2) is prepared by polymerizing only methyl methacrylate corresponding to the monomer (1). The polymer (3) is prepared by polymerizing a mixture of ethyl acrylate (13 parts) and methyl methacrylate (7 parts)

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corresponding to the monomer (II). The polymer (I) is a random copolymer obtained by polymerizing a mixture of the monomers constituting the polymer sample (1).

5 Each polymer sample (5 parts) is admixed with polyvinyl chloride (average polymerization degree: 660) (100 parts), tin acetyl mercapride stabilizer (1.5 parts), soya-bean oil epoxide (1.5 parts), butyl stearate (1.0 part).

TABLE 1.

Preparation of Polymer (B)		Comparative Examples			
Polymer sample No.	Amount of the monomer constituting the Monomer (I)	Only monomer (I)	Only Monomer (II)	(3)	(4)
Amount of the monomers constituting the polymer (B) (I+II)	Amount of the monomer constituting the monomer (I)	100	0	0	0
	(b') Ethyl acrylate	0	65	(13)	0
	(a') Methyl Methacrylate	0	35	(87)	0
Percent (%) of (b') in Monomer (II)	65	—	65	—	—
Ratio (I)/(II of the polymer (B))	80/20	100/0	0/100	—	—
Subcomponent of component B					

and aliphatic acid polyglycol ester (0.5 parts), and the resultant mixture is subjected to the following test. Results are shown in Table 1.

Note 1) Cloud value cannot be measured owing to a large amount of non-gelatinized substances on the transparent plate.

Note 2) Cloud value cannot be measured owing to white turbidity on the transparent plate.

TABLE 1 continued

Workability		Properties of the end composition					
Transparency	Non-gelatinized substance	None	A substantial amount	None	A substantial amount	None	None
Period for gelation (minute)	0.3	1.5	1.0	1.0 <	4.0	4.0	4.0
Degree of gelation	1	2	2	2	2	2	4
Percent transmission of total rays (%)	77.9	66.8	3.0	77.0	73.0	73.0	73.0
Cloud value (%)	3.5	Note 1) —	Note 2) —	3.5	4.5	4.5	4.5
Percent transmission of single wave length							
T400 (%)	51.5	2.5	0	48.0	43.5	43.5	43.5
T600 (%)	75.5	55.0	0	73.0	68.0	68.0	68.0

The workability is determined by working a sample (55.0g) at 160°C of the mixer temperature with a Brabender Plastograph tester.

5 The period for gelatinization represents the maximum time (minutes) of the blending resistance after the start of working. As the period becomes shorter, working is more easy and gelatinization is more rapid. The non-gelatinized substance (known as "fish eye") is obtained by blending the composition for 10 minutes after attaining the maximum blending resistance, removing the sample, elongating it to a thickness of below 0.3mm, with a roll, and determining the resultant elongated sheet with the naked eye. The degree of gelatinization is determined by estimating the transparency with the naked eye as compared to the transparency of a control sample. When 10 gelatinization is not very well achieved, the inside of the vinyl chloride resin composition has some hollow spaces which reduce trans-

parency. A reduced number of such spaces shows a more advanced degree of gelatinization. The workability is determined as shown above.

The transparency is obtained by blending the composition at 150°C for 5 minutes with a roll, pressing it at 160°C for 15 minutes to prepare a plate 3mm thick and determining the transparency of the plate. The percent transmission of total rays and the cloud values are measured according to JISK—6714. A larger number for the percent transmission of total rays shows better transparency and a smaller number for the cloud value shows better transparency.

The percent transmission of single wavelength is determined by means of a spectrophotometer with respect to visible rays of 400 m μ and 600 m μ , and the values are indicated as T400 and T600 respectively. In particular, in admixtures of a methacrylic acid

ester resin and a vinyl chloride resin a bluish turbidness is frequently caused to appear. The degree of such turbidness can be determined by the T400 value. The measured value of T600 indicates an inclination similar to the value of the percent transmission of total rays, and from this value the transparency can be evaluated. With respect to either T400 or T600, a greater value means a better transparency. (The above-mentioned blending, test piece-preparing, measuring and evaluating methods will apply to samples given in subsequent Examples.

Accordingly, it is evident from the above results that the polymer sample (1) of this invention is better in workability and transparency than the control polymer samples (1) and (2). Still, the polymer sample (1) of this invention is excellent in all aspects of workability including in particular the problem of non-gelatinized substances, and shows good results with respect to transparency in comparison with the control polymer sample (3) of the random copolymer having the same composition of monomers as that of the present invention. In comparison with the composition which is free of polymer materials, the present polymer sample (1) has good workability. Thus, the composition of polyvinyl chloride containing the polymer sample (1) of this invention shows a short period for gelatinization and favorable workability without the presence of non-gelatinized substances. The present composition is excellent in transparency, showing low cloud value and little turbidity in T400.

Example 2.

The following samples, prepared by mixing vinyl chloride resin with the polymer (B), are subjected to the same tests as in Example 1, in order to examine what differences are produced by the methods for preparing polymers (B). Sample 1 (from Example 1) is considered to have a partially graft or block structure. The polymer sample (J) is obtained

when a latex (2) and a latex (3) (each average granular diameter: almost 1000Å) are blended in a ratio of 8:2 in order to make the same composition as the polymer sample (1), and the resultant blend is coprecipitated with sodium chloride, washed with water and dried to give a test sample. Control sample (K) is prepared by coagulating each of latex samples (2) and (3), drying to make a granular powder, and blending the two powders in a ratio of 8:2 in order to make the same composition as the polymer sample (1).

Control sample (L) is prepared by using the same total monomers as those of the polymer sample (1) and polymerizing (I) and (II) in the contrary order. Accordingly, a mixture of ethyl acrylate (13 parts) and methyl methacrylate (7 parts) (corresponding to the polymer (II)) is added over an hour to the polymerization reaction described in Example 1, and the resultant mixture is stirred with heating for 1 hour to complete the polymerization substantially. Methyl methacrylate (80 parts) (corresponding to the polymer (1)) is added thereto in 4 hours, and the resultant mixture is kept at 60°C for 1.5 hours, salted out to coagulate and dried to give the control sample (L).

The above 4 samples are arranged to have almost the same granular distribution as that of the polyvinyl chloride used, in view of the influence of granular size with regard to the remaining non-gelatinized substance.

Results are shown in Table 2.

Note 1) Cloud value cannot be measured owing to a big amount of non-gelatinized substance on the transparent plate.

It is evident from the above results that the composition of the present invention can produce a product free of non-gelatinized substance, having been gelatinized in a short time, and having a good degree of gelatinization, according to the method for preparing the polymer (B). The most favourable is the polymer sample (1), and next is the polymer sample (J).

TABLE 2.

		Example of this invention		Comparative Examples	
Sample Mark		(I)	(J)	(K)	(L)
		Monomer (I) polymerized in emulsion, and monomers (II) added to polymerize therewith in the same phase	(I) and (II) polymerized in emulsion respectively, treated respectively and blended in latex	(I) and (II) polymerized in emulsion respectively, treated re-spectively and blended in powder	Monomers (II) polymerized in emulsion and monomer (I) added to polymerize therewith
Preparation of Polymer (B)					
Amount of the monomers constituting the polymer (B) (I+II)	Amount of monomers constituting the monomer (I)	Methyl methacrylate	80	80	80
		b' Ethyl acrylate	13	13	13
		a' Methyl Methacrylate	7	7	7
Percent of (b') in the monomer (II)		65	65	65	65
Ratio of (I)/(II) in the polymer (B)		80/20	80/20	80/20	80/20
Subcomponents of component B					

TABLE 2 Continued.

Properties of the end composition						
Workability	Non-gelatinized substance	None	None	Quite a lot found	Quite a lot found	Quite a lot found
Time for gelation (minute)	0.3	0.4	1.5	1.3	1.3	1.3
Degree of the gelation	1	1	2	2	2	2
Transparency	Percent transmission of total rays (%)	77.9	77.0	71.0	75.3	75.3
	Cloud value (%)	3.5	3.8	Note 1)	—	4.5
	Percent transmission of single wave length T400 (%)	51.5	50.7	5.3	47.0	47.0
	T600 (%)	75.5	74.3	57.3	72.0	72.0

non-gelatinized substances and take a long period for gelatinization owing to too small amount of (a') in the monomer (II). Control polymer samples (10) and (11) lack in transparency and are apt to leave non-gelatinized substance owing to the presence of only (b') and absence of methyl methacrylate (a') in the polymer (II). The polymer sample (8) using another monomer in the monomer (II) is within the scope of the composition of this invention exhibits equivalent results. It is evident that each of the polymer samples of this invention are excellent in workability and transparency.

Example 3.

Polymer samples (5) to (12) are obtained by affecting the same procedures as the first procedure in Example 1, using the amounts of each monomer of (I) and (II) in the polymer (B) as in Table 3 and changing the ratio of acrylic acid ester or methacrylic acid ester (except methyl methacrylate) (b') and methyl methacrylate (a') in (II). The tests are performed as in Example 1. Results are shown in Table 3. Results of the polymer sample (1) obtained in Example 1 is referred to therein.

15 Control polymer samples (9) and (12) leave

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TABLE 3.

		Example of this invention						Comparative Examples		
Polymer sample No.		(1)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Amount of monomers constituting the polymer (B) (I + II)	Amount of the monomer constituting the monomer (I)	Methyl methacrylate	80	80	80	70	80	70	90	80
	Amount of monomers constituting the monomer (II)	b' Ethyl acrylate	13		10	10	13	10	10	5
		b' n-buryl methacrylate		13	5	10			10	
		c' Acrylonitrile				2				
		a' Methyl methacrylate	7	7	5	10	5	20		15
Percent (%) of (b') in the monomer (II)		65	65	75	67	65	33	100	100	25
Ratio (I)/(II) in the polymer (B)		80/20	80/20	80/20	70/30	80/20	70/30	90/10	80/20	80/20

Subcomponents of component B

TABLE 3 Continued.

Properties of the end composition									
Workability	Non-gelatinized substance	None	None	None	None	Found	Scarce-ly found	Found	Rather much found
Time for gelation (minute)	0.3	0.4	0.5	0.4	0.4	0.7	1.0	4.0	1.3
Degree of the gelation	1	1	1	1	1	1	2	2	2
Transparency	Percent transmission of total rays (%)	77.9	78.0	77.0	77.3	77.0	75.2	70.0	71.3
	Cloud value (%)	3.5	3.5	3.6	3.0	3.4	3.5	9.1	4.5
	Percent transmission of single wave length								4.5
	T400 (%)	51.2	50.0	51.0	51.0	51.5	46.5	44.0	45.0
	T600 (%)	75.5	75.5	76.7	76.0	75.0	74.0	48.5	70.5
									73.0

Example 4.

The polymer samples (13)–(19) are obtained by repeating the same first procedure as in Example 1, using each amount of monomers of (I) and (II) in the polymer (B) as shown in Table 4, and changing the ratio of (I) and (II) in the polymer (B). The tests are carried out similarly to Example 1. Table 4 shows the results. Results of the polymer

samples (1) and (2) in Example 1 are referred to therein.

Not: 1) Cloud value cannot be measured owing to white turbidity on the transparent plate.

It is apparent from the transparency of the samples as given in Table 4 that the amount of monomer (I), should be 50 to 99 parts, and the amount of monomer (II) should be 1 to 50 parts, in the polymer (B).

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TABLE 4.

		Example of this invention						Comparative examples		
		(13)	(1)	(14)	(15)	(16)	(2)	(17)	(18)	(19)
Amount of monomers constituting the polymer (B) (I+II)	Amount of the monomer constituting the monomer (I)	Methyl methacrylate	95	80	80	60	100	40	40	20
	Amount of monomers constituting the monomer (II)	b' Ethyl acrylate	4	13	4	7		40	24	
		b' <i>n</i> -butyl methacrylate			3	6			18	
		b' Ethyl methacrylate					15			30
		b' <i>n</i> -butyl acrylate					15			30
		a' Methyl methacrylate	1	7	3	7	10		20	18
								20	18	20
Percent (%) of (b') in the monomer (II)		75	65	70	65	75	—	67	70	75
Ratio (I/II) in the monomer (B)		95/5	80/20	90/10	80/20	60/40	100/0	40/60	40/60	20/80

Subcomponents of component B

TABLE 4. Continued.

Properties of the end composition									
Workability	Non-gelatinized substance	Scarce- ly found	None	None	None	Very much found	None	None	None
Time for gelation (minute)	1.1	0.3	0.7	0.5	0.8	1.5	1.0	1.5	1.0
Degree of the gelation	1	1	1	1	1	2	1	2	3
Transparency	Percent transmission of total rays (%)	78.9	77.9	78.7	78.5	72.3	69.8	41.7	50.5
	Cloud valve (%) value	4.0	3.5	2.9	3.0	4.0	Note 1)	16.7	5.8
	Percent transmission of single wave length	T400 (%)	51.0	51.5	52.5	52.0	49.7	2.5	6.5
		T600 (%)	74.5	75.5	77.5	77.5	70.0	55.0	38.0
								21.3	0
								48.0	0

Example 5. The polymer sample (1) of Example 1 is prepared as in Example 1, and the following tests are carried out. Polyvinyl chloride is used as a comparative example.

1) Polyvinyl chloride (average polymerization degree: 1040) (100 parts), tin mercaptide stabilizer (3 parts), butyl stearate (1 part) and the polymer sample (1) (10 parts) are admixed, and the resultant mixture is blended at 140°C, and may be easily rolled onto a roll. A transparent sheet is obtained. This sheet is folded but not split thereby. The control composition containing no polymer sample (1) requires a larger time for coiling around the roll at 140°C, and the sheet obtained splits on bending owing to lack of gelatinization. To obtain a sheet having a strength comparable to the previous sheet, the composition must be rolled at 155°C.

When polyvinyl chloride (average polymerization degree: 2500) is used, a difference in rolling temperature, about 15°C, for obtaining a sheet having sufficient strength, is observed.

2) The composition of sample (1) (i.e. Polymer B only) is adopted, but polyvinyl chloride (average polymerization degree: 760) is utilized. The resultant mixture is blended at 155°C with a roll for 5 minutes to give a sheet of 0.5mm thick. This sheet is heated at 160°C and subjected to vacuum molding, wherein deep draw is available. The control composition containing no polymer sample (1) is broken at the vacuum molding, whereby it cannot be molded. The sample sheet is pressed at 165°C, and the dumbbell test chip (JS 2) obtained by cutting is subjected to an elongation test for breaking elongation at 140°C at a tensile rate of 100 mm/minute. The composition containing the polymer sample (1)

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shows 200% elongation and the composition free of the polymer sample (1) shows 65% elongation.

3) The polymer sample (1) (2 parts) is added to a mixture of polyvinyl chloride (average polymerization degree: 660) (87 parts), impact resistance increasing agent (copolymer resin of methyl methacrylate - butadiene - styrene: Kane Ace B-12 prepared by Kanefuchi Chemical Industry, Ltd.) (13 parts), tin octyl mercaptide stabilizer (1.5 parts), soybean oil epoxide (1.5 parts), butyl stearate (1.0 part) and aliphatic acid polyglycol ester (0.5 parts), and the resultant mixture is subjected to blow molding. The composition containing the polymer sample (1) (2 parts) produces bright blow bottles having uniform appearance 5 hours after the start of blow molding and being free of non-gelatinized substance. The composition containing no polymer sample (1) produces bottles without brightness on the surface 1 hour after the start of blow molding. This fact shows that the composition of this invention containing the polymer sample (1) can produce the bottles for a long time uniformly.

4) The polymer sample (1) (5 parts) is added to a mixture of vinyl chloride copolymer resin (average polymerization degree: 800) (100 parts) containing 8% vinyl acetate, tin mercaptide stabilizer (3 parts) and butyl stearate (1 part), and the resultant mixture is subjected to the Brabender plastograph tester to determine the workability, wherein 0.1 minute is required for gelatinization. The blend is free of non-gelatinized substance and is well-gelatinized. The composition containing no polymer sample (1) takes 1 minute for gelatinization, and the blend is ill-gelatinized.

5) The polymer sample (1) (3 parts) is added to a mixture of polyvinyl chloride later chlorinated (average polymerization degree: 800) (100 parts) containing 66% of chlorine, tin stabilizer (3 parts) and metal soap (3 parts), and the resultant mixture is subjected to an extruder of 65 mm to extrude hollow pipes, whereby there can be obtained pipes having favorable appearance on the surface and being well-gelatinized. The composition without polymer sample (1) affords pipes having a dull surface and having many rough parts. It is evident that the composition of this invention containing polyvinyl chloride later chlorinated can be easily gelatinized.

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Example 6.

A reactor equipped with a stirrer is charged with an aqueous solution of 2 parts of sodium

dodecylbenzenesulfonate and 0.1 part of ammonium persulfate, and water is added thereto until the total amount of water is 200 parts. Oxygen contained in the inside atmosphere of the reactor and in the charge is removed, and the temperature of the solution is elevated to 60°C. under agitation, and a monomeric mixture consisting 75 parts of methyl methacrylate and 10 parts of n-butyl methacrylate (corresponding to constituent (I) of the polymer (B)) is added thereto over a period of 4 hours and 15 minutes. After completion of the addition of the monomeric mixture, the heating under agitation is continued for 1 hour to complete substantially the polymerization. Then, a monomeric mixture consisting of 5 parts of methyl methacrylate and 10 parts of ethyl acrylate (corresponding to constituent (II) of the polymer (B)) is added to the reaction mixture over a period of 45 minutes, and after completion of the addition of the monomeric mixture, the reaction mixture is maintained at 60°C. for 1 hour and 30 minutes, and then it is cooled. The conversion to polymer is 99.3%. The resulting latex is salted out with sodium chloride to coagulate it, filtered, washed with water and dried to obtain 98 parts of a polymer sample (20) corresponding to the two-staged polymerization product B. The polymer sample (20) has a specific viscosity of 1.65 measured at 30°C. in a benzene solution of a polymer concentration of 0.4g/100 cc.

Comparative polymer samples (21) to (23) are obtained by conducting similar polymerization procedures. In polymer sample (21) only 88.24 parts of methyl methacrylate and 11.76 parts of n-butyl methacrylate corresponding to constituent (I) of polymer sample (20) are copolymerized. In polymer sample (22), only 33.33 parts of methyl methacrylate and 66.67 parts of ethyl acrylate corresponding to constituent (II) of polymer sample (20) are copolymerized. In polymer sample (23), all the monomers constituting polymer sample (20) are collectively subjected to the random polymerization according to an ordinary polymerization method.

Each polymer sample in an amount of 5 parts is blended with 100 parts of a polyvinyl chloride (having an average degree of polymerization of 660) 1.5 parts of an octyl tin mercaptide stabilizer, 1.5 parts of soybean oil epoxide, 1 part of butyl stearate and 0.5 part of a polyglycol ester of a fatty acid, and the resulting composition is subjected to the following tests. Results are shown in Table 5.

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TABLE 5.

		Example of this invention		Comparative Examples		
		emulsion polymerization of monomers (I) and subsequent emulsion polymerization of monomers (II) in same system		only monomers (I) are polymerized	only monomers (II) are polymerized	random co-polymer obtained by polymerizing monomers (I) and (II) free of polymer (B)
Process of preparation of polymer (B)		(20)	(21)	(22)	(23)	
Monomers constituting polymer (B) (I + II) (amounts)	Monomers constituting (I)	methyl methacrylate (a) n-buty1 methacrylate (b)	75 10	88.24 11.76	0 0	(80) (10)
	Monomers constituting (II)	methyl methacrylate (a') ethyl acrylate (b')	5 10	0 0	33.33 66.67	(10)
Ratio (%) of constituent (I) in polymer (B)		85	100	0	—	—
Ratio (%) of (b') in constituent (II)		66.7	—	66.7	—	—

TABLE 5. Continued.

Properties of final composition						
Workability	Presence of ungelled portions	not observed	considerably observed	not observed	considerably observed	not observed
	Time for gelation (minutes)	0.5	1.3	0.8	1.0	4.0
Degree of gelation	1	1	3	1	1	4
	Percent transmission of total rays (%)	80.0	81.5	2.8	79.0	73.0
Transparency	Haze value (%)	2.6	2.8	(note 1)	2.6	4.5
	Percent transmission of single wavelength	55.0	57.5	0	53.2	43.5
T400 (%)		78.0	80.0	0	76.6	68.0

Note 1: Haze value cannot be measured owing to white turbidity on the transparent plate.

From the above results it is seen that the polymer sample 20 when incorporated in a resin of this invention, is superior to the comparative polymer sample 21 with respect to the presence of ungelled portions and the time for gelation, the polymer sample 20 is superior to the comparative polymer sample 22 with respect to the time for gelation and the degree of gelation and much superior in transparency, ^{the presence}

5 parative polymer sample 21 with respect to the presence of ungelled portions and the time for gelation, the polymer sample 20 is superior to the comparative polymer sample 22 with
 25 for gelation with an advanced degree of gelation and without any ungelled portions, and has an excellent transparency showing a low haze value and a low turbidity in T400.

respect to the time to gelation and the degree of gelation and much superior in transparency, and that it is superior as regards the presence of ungelled portions, the time for gelation and transparency to the comparative random copolymer sample 23 formed from the same monomer composition. Furthermore the polymer compositions consisting of polymer sample 20 and polyvinyl chloride, according to this invention are superior to those constituting polyvinyl chloride alone, in both workability and transparency. In short, the polyvinyl

Example 7. The following samples are prepared and tested in the same manner as in Example 6 in order to examine what difference is brought about by the difference in the method of pre-

Sample (J): Data of the polymer sample (20) obtained in Example 6 are adopted. It is construed that the sample has partially a grafted or blocked structure (two-staged polymerization product).

5 Sample (K): Latices of sample polymers (21) and (22) (each having an average particle size of about 1000 \AA) are blended at a ratio of 85:15 so as to attain the same composition ratio as in the polymer sample (20), and the resulting latex mixture is coprecipitated with sodium chloride, washed with water and dried (polymeric mixture blended in the latex state).

10 Comparative sample (L): Latices of sample polymers (21) and (22) are separately coagulated, washed with water and dried to obtain fine powders. Then, the powders are blended at a ratio of 85:15 so as to attain the same composition ratio as in the sample polymer (20) (powdery blend).

15 Comparative sample (M): A sample is prepared by employing the same monomer composition as in the sample (20) but revers-

ing the order of the emulsion polymerization of monomeric mixtures (I) and (II). More specifically, monomers constituting the component (II) of the sample (20) are at first subjected to the emulsion polymerization and then in the presence of the resulting polymer latex monomers constituting the component (I) are polymerized. The resulting polymer is coagulated, washed with water and dried to obtain a sample (contrary two-staged polymerization product.)

20 In view of influences of the particle size on occurrence of ungelled portions, in each of four samples (J) to (M), the particle size distribution is so adjusted that it is almost the same as the size distribution of the polyvinyl chloride used.

25 Results are shown collectively in Table 6.

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TABLE 6.

Sample No.		Example of this invention		Comparative Examples	
		(J)	(K)	(L)	(M)
		emulsion polymerization of monomers of (I) and subsequent polymerization of monomers of (II) in same system	monomers of (I) and (II) are emulsion polymerized separately, resulting polymers are treated separately, and they are mixed in powdery state	monomers of (I) and (II) are emulsion polymerized separately, resulting polymers are treated separately, and they are mixed in powdery state (powderly mixture)	monomers of (I) and (II) are emulsion polymerized and monomers of (I) are polymerized in same system (contrary two-staged polymerization product)
		Process of preparation of polymer (B)			
Monomers constituting polymer (B) (amounts)	Monomers constituent (I)	methyl methacrylate (a) n-buty1 methacrylate (b)	75 10	75 10	75 10
	Monomers constituent (II)	methyl methacrylate (a') ethyl acrylate (b')	5 10	5 10	5 10
Components of polymer (B)					

TABLE 6 Continued

Properties of resulting composition		85	85	85	85	85
Ratio of constituent (I) in polymer (B) (%)						
Ratio of (b') in constituent (II) (%)		66.7		66.7		66.7
Workability	Presence of ungelled portions		not observed		considerably observed	considerably observed
Time for gelation (minutes)		0.5		0.6		2.0
Degree of gelation		1		1		1
Transparency	Percent transmission of total rays (%)	80.0		79.8		76.8
	Haze value (%)	2.6		2.8		3.5
Percent transmission of single wavelength	T400 (%)	55.0		53.4		50.0
	T600 (%)	78.0		77.0		74.2

From the above results, it is seen that the polymer (B) prepared according to the process of this invention gives an excellent composition as compared with comparative polymer samples in the respect that ungelled portions are not observed and the time for gelation is short, i.e. the gelation-accelerating effect is high.

Among the above samples, one prepared by the method (I) is most preferred when all the items are taken into consideration collectively.

Example 8.

Procedures of Example 6 are repeated, but changing the kinds and amounts of the monomers of the constituents (I) and (II) of the two-staged polymerization product (3) as indicated in Table 7. The resulting polymer samples are tested in the same manner as in Example 1. Results are shown in Table 7.

Results for the polymer samples (20), (21) and (22) obtained in Example 6 are also shown in Table 7.

TABLE 7.

		Sample of this Invention						Comparative Sample			
Sample No.		(24)	(25)	(20)	(26)	(27)	(21)	(28)	(29)	(22)	
Monomer constituent (I)	Monomers constituting polymer (B) (amounts)	methyl methacrylate (a)	90	80	75	75	60	88.2	37.5	18.5	
		ethylmethacrylate (b)	5	10			10				
		n-buryl methacrylate (b)			10			11.8	2.5	1.5	
		ethyl acrylate (b)				10					
Monomers constituent (II)	Monomers constituent (I)	methyl methacrylate (a')	1	4	5	5	10		20	26.7	33.3
		n-buryl methacrylate (b')				10	10				
		ethyl acrylate (b')	4	6	10		10		40	53.30	66.7
Ratio (%) of constituent (I) in polymer (B)		95	90	85	85	70	100	40	40	20	0
Ratio (%) of (b') in constituent (II)	80	60	66.7	66.7	66.7	—	—	66.7	66.7	66.7	

Components of polymer (B)

TABLE 7 Continued.

Properties of Composition							
Workability	Presence of ungelled portions	hardly observed	not observed	not observed	not observed	considerably observed	not observed
time for gelation (minutes)	1.0	0.7	0.5	0.4	0.4	1.3	0.6
Degree of gelation	1	1	1	1	1	1	2
Transparency	Percent transmission of total rays (%)	77.8	79.0	80.0	79.6	78.3	81.5
	Haze value (%)	2.5	2.6	2.6	2.6	2.7	2.8
Percent transmission of single wave-length (%)	T400	53.0	55.0	55.0	54.2	57.5	12.0
	T600	76.0	78.0	78.0	77.7	76.4	80.0

Note 1: Haze value cannot be measured owing to white turbidity on the transparent plate.

From the results shown above, it is seen that the polymer (B) should be 50—99 parts of the constituent (I) and 50—1 part of constituent (II), because a high transparency can be attained in the resulting composition. It is also seen that the acrylic acid ester or methacrylic acid ester exclusive of methyl methacrylate (b') in the constituent (II) is varied and incorporation of other monomers (c) and (c') copolymerizable with monomers (a) and (b) and monomers (a') and (b') is also examined. Thus there are obtained polymer samples (30) to (39). These samples are tested within the range specified in this invention.

Example 9.

The procedure of Example 6 is repeated but changing the amounts of monomers of constituents (I) and (II) in the two-staged

polymerization product (B) as indicated in Table 8, so as to examine influences of the monomers of the constituent (II) in the polymer (B). More specifically, the ratio of methyl methacrylate (a') and the acrylic acid ester or methacrylic acid ester exclusive of methyl methacrylate (b') in the constituent (II) is varied and incorporation of other monomers (c) and (c') copolymerizable with monomers (a) and (b) and monomers (a') and (b') is also examined. Thus there are obtained polymer samples (30) to (39). These samples are tested in the same manner as in Example 6. Results are shown in Table 8.

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TABLE 8.

TABLE 8 Continued.

		Properties of resulting composition							
		80	85	85	80	80	80	80	80
Ratio (%) of (B) in polymer		80	85	85	80	80	80	80	80
Ratio (%) of (b') in constituent (II)		65	66.7	66.7	95	95	92	0	25
Workability	Presence of ungelled portions	not observed	not observed	not observed	not observed	not observed	considerably observed	observed	not observed
Time for gelation (minutes)		0.6	0.4	0.5	0.5	0.6	0.5	2.3	1.3
Degree of gelation		1	1	1	1	1	1	2	1
Transparency	Percent transmission of total rays (%)	79.2	78.9	78.3	81.5	78.2	77.6	80.0	78.1
	Haze value (%)	2.4	2.7	2.9	2.4	2.6	2.8	3.1	2.7
	Percent transmission of single wavelength T400 (%)	54.2	58.5	51.6	55.4	58.9	51.9	50.3	52.0
T600 (%)		77.8	78.4	76.1	79.7	77.0	77.9	76.2	78.5

Comparative samples (36) and (37) are inferior with respect to the gelation-accelerating effect because of a major content of methyl methacrylate (a') in the constituent (II), and therefore, in these samples there are observed ungelled portions. The comparative sample (38) is inferior in respect to the transparency owing to a minor content of methyl methacrylate (a) in the constituent (I). In the comparative sample (39), the degree of gelation is poor because of the absence of methyl methacrylate (a') in the constituent (II), and also the transparency is inferior. On the other hand, polymer samples of this invention do not bring about such disadvantages. More specifically, as is seen from data of samples (30) to (31), good workability and high transparency can be maintained even if the kind of the acrylic acid ester or methacrylic acid ester exclusive of methyl acrylate is varied. Further, even in the case of polymer samples (32) and (33) formed by employing other copolymerizable monomers, the resulting compositions possess apparently characteristic features and advantages intended in this invention.

Example 10.

The polymer sample (20) is prepared in the same manner as in Example 6, and the following workability tests are conducted. As a comparative sample, compositions free of the polymer sample (20) are also tested.

a) 10 parts of the polymer sample (20) is incorporated into a mixture consisting of 100 parts of a polyvinyl chloride (having an average degree of polymerization of 1040), 3 parts of a tin mercaptide stabilizer and 1 part of butyl stearate, and the mixture is kneaded at 140°C. by means of a roll. The mixture is readily wound around the kneading roll, and there is obtained a transparent sheet. The resulting sheet is not broken or cracked under bending. The comparative composition free of the polymer sample (20) requires a considerable time for winding around the kneading roll at a processing temperature of 140°C. The sheet obtained by conducting the kneading at 140°C. is always broken under bending because of an insufficient degree of gelation. In order to obtain a sheet having a sufficient strength from the comparative composition, it is necessary to conduct the roll kneading at 155°C.

Also when a polyvinyl chloride (having an average degree of polymerization of 2500) is used, there is a difference of kneading temperature of about 15°C. for obtaining a sheet having a sufficient strength between the composition containing the polymer sample (20) and the comparative composition free of the polymer sample (20). Thus, in the composition containing the polymer sample (20), the processing temperature can be lowered.

b) 10 parts of the polymer sample (20) is incorporated into a mixture having the same composition as in a) except that a polyvinyl

chloride (having an average degree of polymerization of 760) is used, and the resulting mixture is kneaded at 155°C. for 5 minutes by means of a roll to obtain a sheet of 0.5 mm thickness. The sheet is heated to 160°C. and subjected to vacuum molding. In this molding, deep drawing can be attained. In the comparative composition free of the polymer sample (20), occurrence of breakages is extreme in the vacuum molding, and therefore, accomplishment of the molding is impossible. These sheet are pressed at 165°C. and dumbbell test pieces of JIS 2 are prepared therefrom by cutting. With respect to these test pieces, the elongation at breakage is determined at 140°C. at a pulling rate of 100 mm/min. The composition containing the polymer sample (20) shows a 200% elongation, whereas the comparative composition free of the polymer sample (20) shows only a 65% elongation.

c) 2 parts of the polymer sample (20) is incorporated in a mixture consisting of 87 parts of a polyvinyl chloride (having an average degree of polymerization of 660), 13 parts of an impact resistance enforcing agent (methyl methacrylate - butadiene - styrene copolymer resin: Kane Ace B-12 manufactured by Kanegafuchi Chemical Industry), 1.5 parts of an octyl tin mercaptide stabilizer, 1.5 parts of soybean oil epoxide, 1 part of butyl stearate and 0.5 part of a fatty acid polyglycol ester, and the resulting composition is subjected to the blow molding test. In the composition containing the polymer sample (20), even after the blow molding operation has been continued for 5 hours, there is not observed any change in appearance in blow-molded bottles which are free of ungelled portions and have a lustrous surface. In contrast, in the composition free of the polymer sample (20), in about 1 hour from the initiation of the blow molding bottles come to have no luster or brightness on the surface. This fact means that the resin composition of this invention containing the polymer sample (20) makes it possible to conduct the blow molding stably for a long period of time.

d) 5 parts of the polymer sample (20) is incorporated into a mixture consisting of 100 parts of a vinyl chloride-vinyl acetate copolymer resin of a vinyl acetate content of 8% (having an average degree of polymerization of 800), 3 parts of a tin mercaptide stabilizer and 1 part of butyl stearate, and when the resulting composition is subjected to the Brabender plastograph test, it is found that the time for gelation is 0.1 minute. The product obtained by kneading the composition is well gelled and free of ungelled portions. In the comparative composition free of the polymer sample (20), the time for gelation is as long as 1.0 minute, and in the kneaded product the degree of gelation is insufficient.

e) 3 parts of the polymer sample 20 is incorporated into a mixture consisting of 100

parts of a post-chlorinated polyvinyl chloride of a chlorine content of 66% (having an average degree of polymerization of 800), 3 parts of a lead stabilizer and 3 parts of a metal soap, and the composition is molded into hollow pipes by employing an extruder of a diameter 65mm. Thus, there can be obtained pipes having a good surface condition and a sufficient degree of gelation. From the comparative composition free of the polymer sample 20, there are obtained pipes having no brightness on the surface with opaque portions and a great number of convexities and concavities. Thus it is evident that in the composition of this invention, even if a post-chlorinated polyvinyl chloride is used as the polyvinyl chloride component, an excellent gel effect is attained and a sufficient degree of gelation is obtained.

20 WHAT WE CLAIM IS:—

1. Vinyl chloride resin composition comprising
 - A. 100 parts by weight of a vinyl chloride resin, which comprises polyvinyl chloride, a copolymer having at least 80% vinyl chloride with a monomer copolymerizable therewith, or a post-chlorinated polyvinyl chloride or a combination thereof;
 - B. 0.1 to 100 parts by weight of a two stage polymerization product obtained by polymerizing (I) 50 to 99 parts by weight of methyl methacrylate or a first monomeric mixture comprising a major proportion of methyl methacrylate, and a minor proportion of acrylic acid ester and/or methacrylic acid ester, excluding methyl methacrylate, and then polymerizing in the presence of the resulting polymer latex, (55) 50 to 1 parts by weight of a second monomeric mixture comprising a major proportion of acrylic acid ester and/or methacrylic acid ester, excluding methyl methacrylate, and a minor proportion of methyl methacrylate, wherein said first and second monomeric mixtures comprise other monomers of up to 20 weight percent of each such total monomer mixture.
 2. Composition of claim 1, wherein said acrylic acid esters and methacrylic acid esters are selected from methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, chloroethyl acrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, and chloroethyl methacrylate, and mixtures thereof.
 3. Composition of claim 1, wherein said acrylic acid esters and methacrylic acid esters are selected from methyl acrylate, ethyl acrylate, n-butyl acrylate, ethyl methacrylate, n-butyl methacrylate and mixtures thereof.
 4. Composition of claim 1 wherein said other monomers are selected from unsaturated nitriles, vinyl esters, and monomers containing in the molecule two or more double bonds, and mixtures thereof.
 5. Compositions of claim 1, wherein said

other monomers are selected from acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate, monoethylene glycol dimethacrylate, diethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and mixtures thereof.

6. Composition of claim 1 wherein the specific viscosity (measured at 30°C in benzene solution at a polymer concentration of 0.4 gm/100cc) of said two stage polymerization product is at least 0.1.

7. Composition of claim 6, wherein said specific viscosity is at least 0.5.

8. Composition of claim 1, wherein said polymerization product is kneaded with said vinyl chloride resin.

9. Composition of claim 1, wherein said polymerization of component (B), is emulsion polymerization carried out in the presence of an emulsifier and an initiator.

10. Vinyl chloride resin composition comprising

A. 100 parts of a vinyl chloride resin, which comprises polyvinyl chloride, a copolymer having at least 80% vinyl chloride with a monomer copolymerizable therewith, or a post-chlorinated polyvinyl chloride, or a combination thereof,

B. 0.1 to 100 parts polymeric mixture obtained by mixing in latex state, (I) 50 to 99 parts by weight of a homopolymer of methyl methacrylate or a copolymer formed by polymerizing a monomeric mixture comprising a major proportion of methyl methacrylate, and a minor proportion of acrylic acid ester and/or methacrylic acid ester, excluding methyl methacrylate; and (II) 50 to 1 parts by weight of a copolymer obtained by polymerizing a monomeric mixture comprising a minor proportion of methyl methacrylate and a major proportion of acrylic acid ester and/or methacrylic acid ester, excluding methyl methacrylate, and then coagulating the resulting mixture wherein said monomeric mixtures forming both copolymers comprise other monomers of up to 20 weight percent of each such total monomer mixture.

11. Composition of claim 10, wherein said acrylic acid esters and methacrylic acid esters are selected from methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, chloroethyl acrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate and chloroethyl methacrylate, and mixtures thereof.

12. Composition of claim 10, wherein said acrylic acid esters and methacrylic acid esters are selected from methyl acrylate, ethyl acrylate, n-butyl acrylate, ethyl methacrylate, n-butyl methacrylate and mixtures thereof.

13. Composition of claim 10, wherein said other monomers are selected from unsaturated nitriles, vinyl esters, and monomers containing in the molecule two or more double bonds, and mixtures thereof.

14. Composition of claim 10, wherein said

other monomers are selected from acrylonitrile, methacrylonitriles, vinyl acetate, vinyl propionate, monoethylene glycol dimethacrylate, diethylene glycol di-methacrylate, polyethylene glycol dimethylacrylate and mixtures thereof.

5 15. Composition of claim 10, wherein the specific viscosity measured at 30°C. in benzene solution at a polymer concentration of 0.4 gm/100cc) of said polymeric mixture is at least 0.1.

10 16. Composition of claim 15, wherein said specific viscosity is at least 0.5.

17. Composition of claim 10, wherein said polymerization of component (B) is emulsion polymerization carried out in the presence of 15 an emulsifier and an initiator.

18. A composition as claimed in claim 1 or claim 10 substantially as described in any one of the specific examples hereinbefore set forth.

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